Field measurement of PAHs in California wheat grain

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Field measurement of polycyclic aromatic hydrocarbons in wheat grain grown in Sacramento and San Joaquin Valleys, California

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Abstract

Wheat grain samples from five different counties in California were analyzed for 2- to 6-ring polycyclic aromatic hydrocarbons (PAHs). PAH profiles were similar for all the samples, but concentrations differed by location. Major PAHs present in the California grain were mainly gas-phase PAHs. Diesel-fueled harvesting operations did not appear to contribute to observed PAH concentration in grain. PAHs in grain most likely came from atmospheric deposition.

Key Words

Polycyclic aromatic hydrocarbons (PAHs), wheat, GC-MS analysis, isotope dilution, dietary exposure

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) emitted primarily from combustion sources can accumulate in the food chain. A number of PAHs are mutagenic and/or carcinogenic to mammals, and PAHs are bioavailable through inhalation, ingestion, and dermal contact (1-4). One route of human exposure to PAHs occurs through dietary exposure as a result of bioconcentration in plants from the environment and subsequent transfer through agricultural food chains. Broiled meats, leafy vegetables and unrefined grains have been reported to have higher concentrations of PAHs (5). Also, since grains are a large part of the average diet, PAHs from grain are a large fraction of the total PAH intake from foods (6, 7). The contamination source for unprocessed grains and vegetables is suspected to be air rather than soil because of the hydrophobic nature of these compounds. To reduce the potential exposure to these toxic compounds, it is important to examine the levels present in unprocessed raw crops. For the current study, 2- to 6-ring PAHs were measured in wheat grain grown in California. Wheat was chosen because products containing wheat are widely consumed in all segments of society.

2. Materials and Methods

Wheat grain samples harvested in June 2001 were obtained from the fields in Chico and Davis located in the Sacramento Valley, and Stockton, Madera, and Corcoran located in the San Joaquin Valley (Table 1). The Sacramento and the San Joaquin Valleys connectively define a vast agricultural region in an airshed that is heavily impacted by continued urban development. Significant sources of reactive organic gases include mobile sources in the Sacramento Valley, and both mobile sources and the production of oil and gas in the San Joaquin Valley (8).

A hard red spring wheat commonly grown in California (cultivar Yolo) was sampled for this study. Wheat was harvested and threshed at individual fields by a diesel fueled plot combine (Wintersteiger GmbH, Austria). In addition to these five samples, wheat plants that were harvested by hand using a sickle were obtained from the same Davis farm to explore possible PAH contamination from the combine operation. Samples were stored in amber glass bottles with Teflon lined caps and kept at -20°C until extraction. For the hand harvested wheat, grains were removed from the husk by gently crushing the wheat with a Teflon pestle.

An isotope dilution method was employed for chemical analysis of PAHs. An internal standard solution was prepared by diluting a mixture of deuterated PAHs ranging from 2- to 6-ring (Cambridge Isotope Laboratories, Andover, MA) in dichloromethane (DCM). In a typical extraction, fifty grams of wheat grain were ground using a commercially available grinder (Commercial blender 7010s, Waring, New Hartford, CT). The internal standard solution was added to the sample prior to extraction. The sample was extracted with DCM by sonication (Model 5510R, Branson Ultrasonics, Danbury, CT) for 30 minutes. The extract and solid matter were separated by filter paper and the filtration residue was extracted a second time for another 30 minutes. The filtrate from the first and second extraction was further filtered through layers of sodium sulfate (anhydrous, 10-60 mesh), Celite (Celite 545, Fisher Scientific), two layers of glass microfibre filters (2.7µm and 1.0µm particle retention, respectively, Whatman International, Maidstone, UK), and PTFE membrane filter (0.5µm pore size, Millipore, Bedford, MA). The extract was concentrated under a nitrogen stream (TurboVap II, Zymark; Hopkinton, MA). Then the extract was purified by gel permeation chromatography where it was loaded onto a glass column

(2.5cm i.d.×15cm length) filled with Bio-Beads S-X3 (Bio-Rad Laboratories, Hercules, CA) and eluted with a mixture of hexane and DCM (1:1, v/v). The first 57.5mL fraction was discarded, and the next 55mL fraction was collected and concentrated under a nitrogen stream. The solvent was exchanged into hexane, and concentrated to 0.5mL. The hexane extract was then added to a column of 10g silica (100-200 mesh nominal, EM Science) saturated with hexane. The column was first eluted with 50mL hexane and then the PAH fraction was eluted in a 50mL mixture of hexane and DCM (9:2, v/v). The PAH fraction was concentrated under a nitrogen stream to approximately 50 to 100μL using toluene as a keeper solvent.

Analysis was conducted by gas chromatography/mass spectrometry (GC-MS) using a Hewlett-Packard (HP) Model 5890 Series II Gas Chromatograph (GC) interfaced to a HP5972 mass selective detector (MSD). The injector was run in splitless mode. The GC was equipped with a DB-5ms fused silica capillary column (30m × 0.25mm i.d. and 0.25μm film thickness). The MSD was run in selective ion monitoring mode. PAH Standard Reference Material (SRM2260, NIST, Gaithersburg, MD) was used to make calibration solutions for quantitation. Compounds measured include naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2,6-dimethylnaphthalene, and 2,3,5-trimethylnaphthalene, (2-ring PAHs), and acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and 1-methylphenanthrene (3-ring PAHs), and fluoranthene, pyrene, benz(a)anthracene, and chrysene (4-ring PAHs), and benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, and dibenz(a,h)anthracene (5-ring PAHs), and indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene (6-ring PAHs), and biphenyl.

Just prior to GC-MS analysis biphenyl-d10 and p-terphenyl-d14 (Cambridge Isotope Laboratories) were added to measure recoveries of internal standards for quality control purposes. Average recoveries for 2-ring, 3-ring, 4-ring, and larger PAHs were approximately 40%, 60%, 70~90% and 70~100%, respectively. Lower recoveries for lighter molecular weight PAHs are thought to be from evaporative losses occurring when concentrating the sample. Three process blanks were analyzed. The

results were reported without blank corrections. Quantitation limit was 18 ng/kg-grain (0.018ppb) for all the compounds.

4. Results and Discussion

Concentrations are reported on a weight basis of field dried grain. Elevated PAH levels were observed in all grain locations especially those from Chico, Stockton, Madera, and Corcoran. The profiles of PAHs measured in grain were similar in all locations and were mainly lighter weight gas-phase PAHs (molecular weight (MW) ≤ 202), whereas concentrations of mostly particle associated PAHs (MW ≥ 228) were considerably lower (less than 0.1 µg/kg or 0.1ppb) (Figures 1 and 2). Gas-phase PAHs present in the highest concentrations were naphthalene, phenanthrene and 2-methylnaphthalene, while particle associated PAHs, benzo(b+j+k)fluoranthenes (coeluted), benzo(e)pyrene, and benzo(g,h,i)perylene, were found in all samples at elevated levels over the blank.

Considerable differences in the concentrations were observed across locations (Figures 3-5). Generally, gas-phase PAHs were higher in grain from the San Joaquin Valley and particle associated PAHs were higher in grain from the Sacramento Valley.

Since diesel exhaust is known to be a considerable source of PAHs (9), particularly the lower molecular weight PAHs (10), we investigated if the near-source and short period emission from a diesel-fueled combine operation could contribute to lower molecular weight PAHs measured in wheat grain. To evaluate this source, PAHs in Davis grain harvested and threshed by a combine were compared to hand harvested grain in Figure 6. PAH levels were the same in hand harvested and machine harvested grain except that naphthalene was higher in hand harvested grain. The reason for the elevated naphthalene is unknown, but one possible explanation is that the hand harvested grain was contaminated with husk material when the husk was crushed and separated from the grain prior to extraction. Based on these initial measurements it appears that diesel-fueled combine operations did not contribute significantly to PAHs in gains used in this study. Therefore, the elevated levels of PAHs in grain are thought to be from

longer exposure times to the ambient air. This may suggest that uptake of airborne PAHs into grain is a diffusion limited process.

According to the monitoring data of several particle associated PAHs at Chico (Sacramento Valley) and Stockton (San Joaquin Valley) by the California Air Resources Board (ARB) (11), ambient air concentrations of particle associated PAHs are higher in Chico than in Stockton, which generally coincides with our observation for grain concentrations (Figure 5). This suggests that higher ambient air concentrations may be related to higher grain concentrations for particle associated PAHs.

Although a major source of PAHs is vehicle exhaust (2, 3, 10), a clear relationship was not observed between grain PAH levels and proximity to major highways (Table 1). However, low levels of particle associated PAHs in grain from Corcoran may be that the farm was located a distance (more than 25km) from busy highway traffic.

Location differences in naphthalene concentration in grain generally coincides with naphthalene emission inventory data compiled by ARB for each county (12), where emissions in 2001 were 666, 287, 138, 1.4, and 68 kg/year in San Joaquin, Madera, Butte, Yolo, and Kings Counties respectively. Except for Kings County, the emission trend is the same as naphthalene concentrations in grain where grain concentrations are in order of Stockton (San Joaquin County) > Madera (Madera County) > Chico (Butte County) >> Davis (Yolo County). This suggests that naphthalene contamination is more of a regional scale issue (i.e., county level) rather than a local scale one. High naphthalene concentrations in grain from Corcoran (Kings County) is not explained by ARB's naphthalene emission inventory data, however, this discrepancy may be explained by some unknown naphthalene sources present in the area. For example, oil wells located in Kings County are not included in the ARB's naphthalene emission inventory. According to a study conducted by Kerr et al. (13) naphthalene has been detected in 100 % of crude oil and condensates (vapor in underground reservoirs but liquid under the atmospheric condition). The mean value of naphthalene concentration in 60 crude oils from around the world was 422.9 mg/kg (ranging from 1.2 to 3700 mg/kg), and it was 1690 mg/kg in 10 condensates (ranging from 200 to 5700 mg/kg).

Fugitive emissions from these oil wells may be contributing to higher naphthalene levels in the ambient air.

PAH profiles in grain and in air are compared in Figure 7 for the Davis samples using atmospheric PAH concentrations measured in August 2003. Naphthalene, methylnaphthalenes, and phenanthrene were major compounds observed both in grain and air. Phenanthrene, 1-methylphenanthrene, fluoranthene, and pyrene were more pronounced in the grain profile compared to the air profile, and it may be that these compounds partition to grain more favorably than naphthalene and methylnaphthalenes due to their higher lipophilicity. Although there appears to be an approximate and constant PAH profile in the grain and air, parallel ambient samples during the growing season would better define the airborne and grain PAH relationship. Further study is needed to explore grain/air relationship for PAHs.

Jones et al. measured PAHs ranging from fluoranthene (4-ring) to coronene (7-ring) in archived wheat grain harvested between 1860 and 1986 in UK (14). They reported marked decline in PAH concentrations in wheat grain, which generally fits with an improvement in air quality. Among the compounds measured fluoranthene had the greatest decline over time where its concentration decreased from 22.8µg/kg (in year 1877-81) to 0.57µg/kg (1979-84). Fluoranthene concentrations in California grain are at a similar level or lower (less than 0.3µg/kg) than the 1979-84 reported values which reflect levels of 20 years ago. Atmospheric PAH levels in California have been declining in recent years due to emission controls for stationary and mobile sources and cleaner fuels for motor vehicles. Lower concentrations in this study compared to the UK study may be due to improved air quality in recent years. Since concentrations of lighter PAHs in wheat grain have not been reported in the literature, a similar trend comparison could not be confirmed with these compounds.

5. Acknowledgement

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196 **Table 1. Description of locations**

Cities (population)	Longitude/ latitude	Major freeways* (distance from the sampling site)	Other potential sources of PAHs (naphthalene emission)**
Chico (pop 60K) (Butte County)	39° 40’ N 121° 50’ W	State highway 99 (3 km NE)	Electric power plants (101 kg/y)
Davis (pop 60K) (Yolo County)	39° 30’ N 121° 45’ W	Interstate 80 (3 km S) Interstate 5 (14 km N) State highway 113 (1 km E)	None
Stockton (pop 244K) (San Joaquin County)	37° 70’ N 121° 30’ W	Interstate 205 (18 km S) Interstate 5 (20 km E) Interstate 580 (18 km S)	Food products (86 kg/y) Glass products (107 kg/y) Wood preserving (45 kg/y) Paper mills (274 kg/y)
Madera (pop 43K) (Madera County)	37° 00’ N 121° 10’ W	State highway 99 (10 km NE)	Electric power plants (218 kg/y)
Corcoran (pop 14K) (Kings County)	36° 05’ N 119° 40’ W	None	None

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198 * Freeways with more than 50,000 annual average traffic in 2001 (15) and located less than
199 25 km from the wheat farms.
200 ** Facilities listed in Emission Inventory by California EPA, Air Resources Board (ARB)
201 that emitted more than 45 kg/year of naphthalene in 2001 (12).
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Figure 1. Volatile and semivolatile PAHs (MW ≤ 202) in wheat grain from Stockton (San Joaquin Valley) and Davis (Sacramento Valley), and in process blank (ng/kg) (Average of n = 3 for Stockton and blank, n = 4 for Davis. Error bars represent ± standard deviation)

Figure 2. Particle associated PAHs (MW ≥ 228) in wheat grain from Stockton (San Joaquin Valley) and Davis (Sacramento Valley), and in process blank (ng/kg) (Average of n = 3 for Stockton and blank, n = 4 for Davis. Error bars represent ± standard deviation)

Figure 3. Comparison of naphthalene concentrations in grain by location (ng/kg) (Average of n=7 for Corcoran, n=4 for Chico and Davis, n=3 for Stockton, Madera and blank. Error bars represent ± standard deviation)

Figure 4. Sum of volatile and semivolatile PAHs (not including naphthalene). Comparison by location (ng/kg) (Average of n=7 for Corcoran, n=4 for Chico and Davis, n=3 for Stockton, Madera and blank.)

Figure 5. Particle associated PAHs in grain. Comparison by location (ng/kg) (Average of n=7 for Corcoran, n=4 for Chico and Davis, n=3 for Stockton, Madera and blank.)

Figure 6. PAHs in grain harvested by combine and by hand
(Grain obtained from Davis. Mean of n = 2 and 4 for hand harvested and machine harvested grain, respectively. For machine harvested grain error bars represent ± 1 standard deviation.)

Figure 7. Comparison of PAH profile in wheat grain and air in Davis, California.
(Machine harvested grain. Air measurement was conducted August 1st to 4th in 2003 in Davis)

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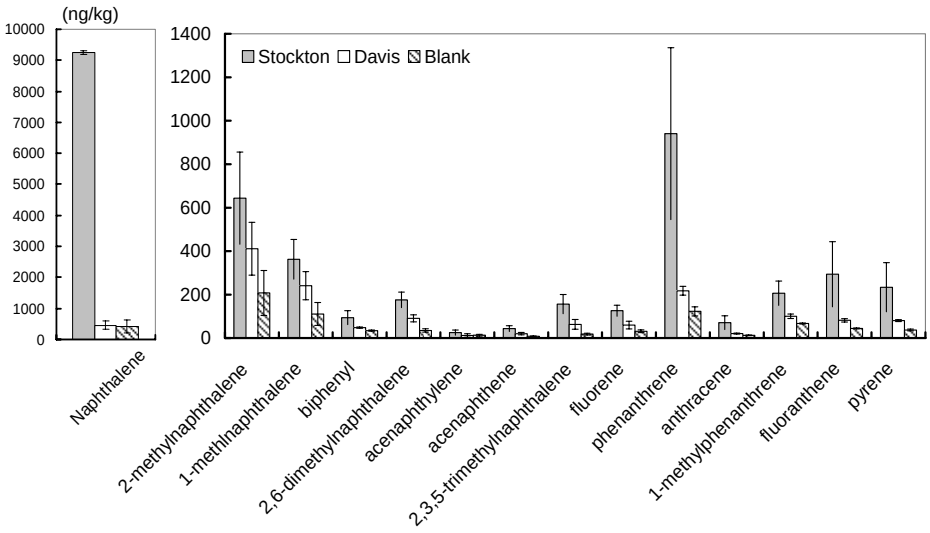

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237 **Valley) and Davis (Sacramento Valley), and in process blank (ng/kg) (Average of n = 3 for Stockton**
238 **and blank, n = 4 for Davis. Error bars represent ± standard deviation)**

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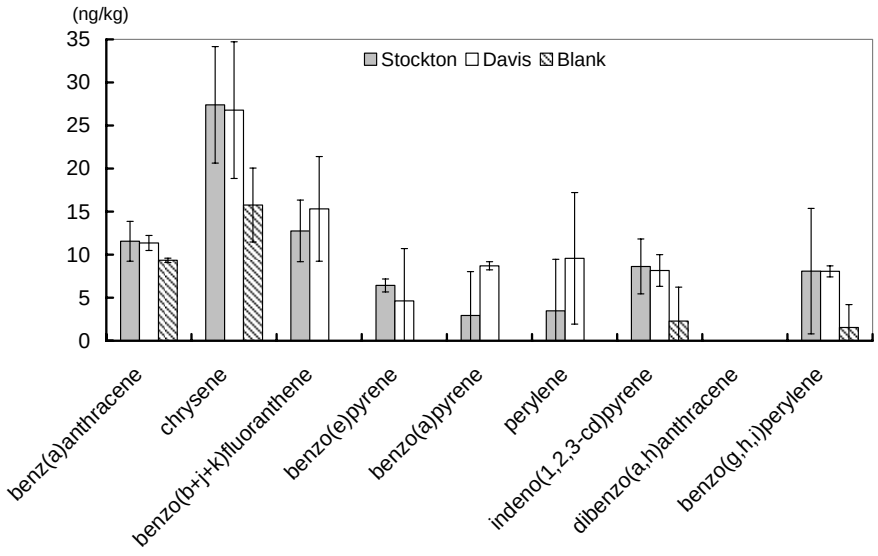

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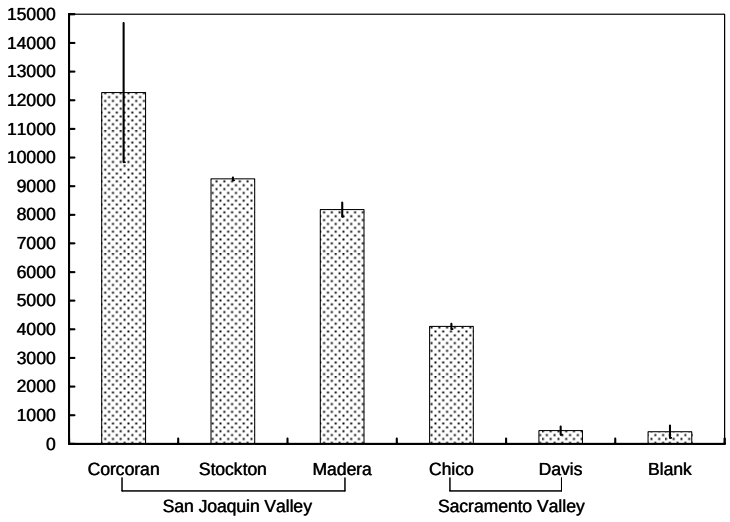
243 **blank, n = 4 for Davis. Error bars represent ± standard deviation)**



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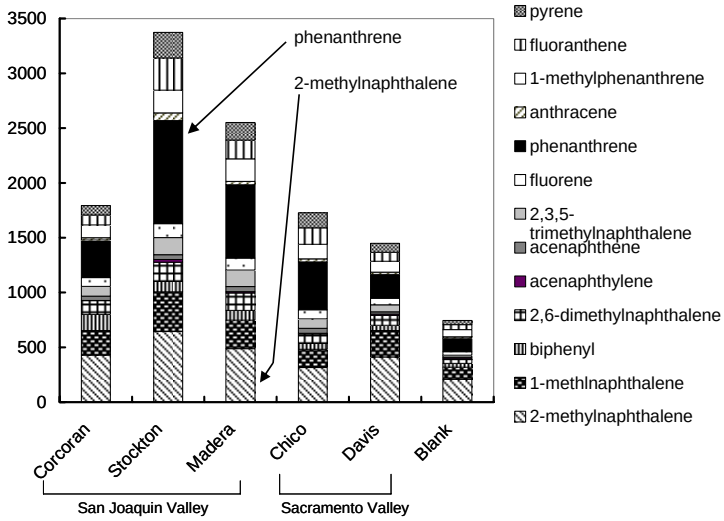

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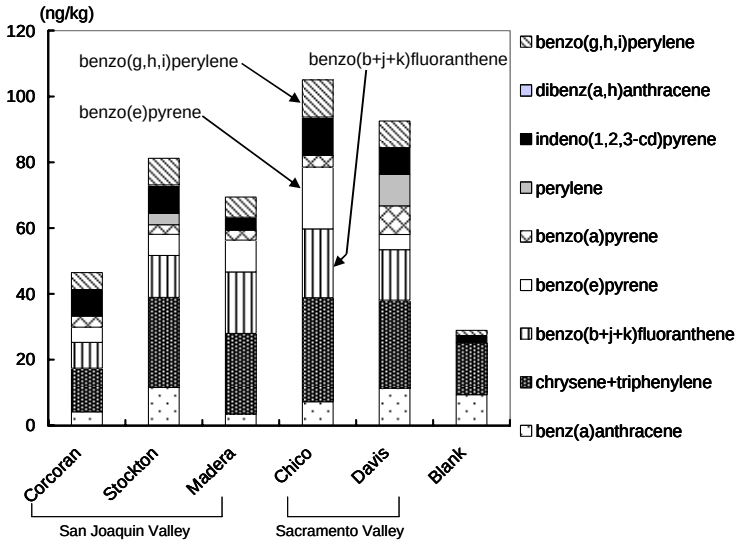

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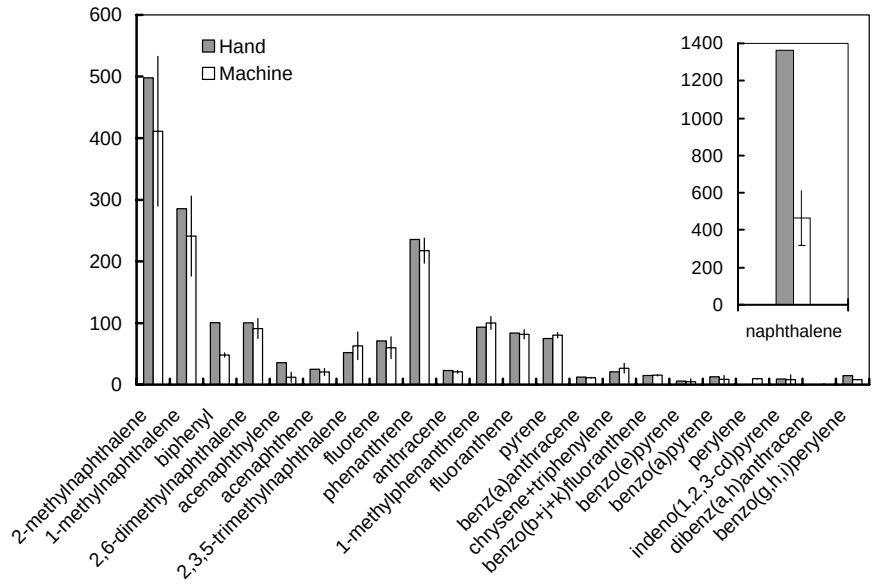
258 **Figure 5. Particle associated PAHs in grain. Comparison by location (ng/kg) (Average of n=7 for**

259 **Corcoran, n=4 for Chico and Davis, n=3 for Stockton, Madera and blank.)**



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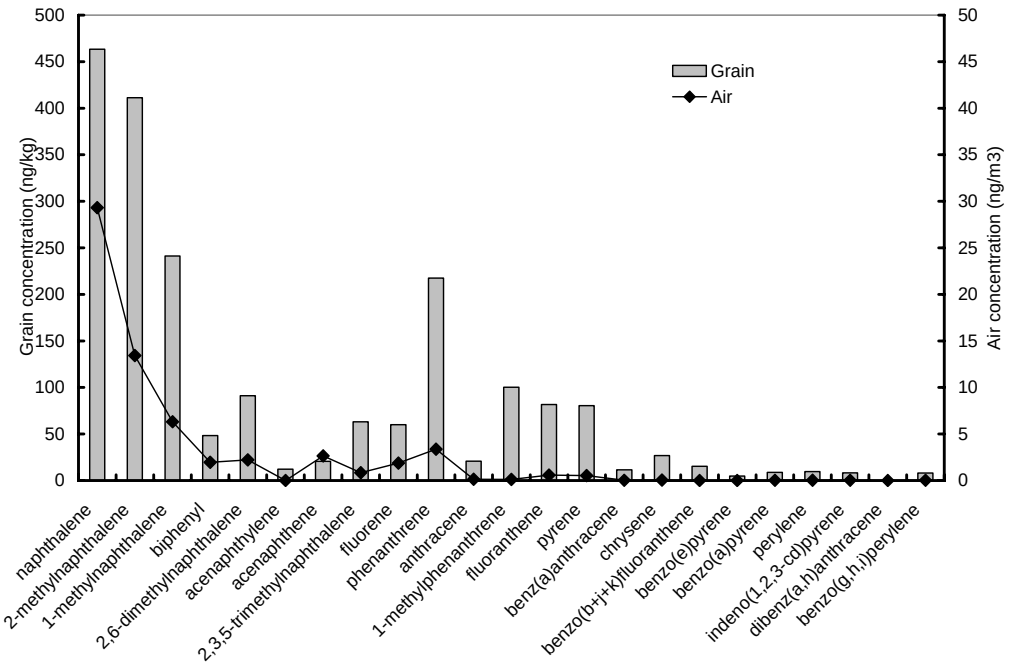

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